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Light thallium isotope ratios in black shales of the 1.73 Ga Wollogorang Formation, Northern Australia

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Eukaryotes likely originated in the oceans ~1.9–1.7 Ga [1,2], however, marine geochemistry at that time remains uncertain. The McArthur Basin was an intracratonic basin that harboured eukaryotic life through the mid-Proterozoic [2] and offers an opportunity to study paleoceanographic conditions during early eukaryotic history.

We report authigenic thallium isotope data ($\varepsilon^{205}Tl_{auth}$; Equation 1) for 60 metres of 1.73 Ga Wollogorang Formation black shales from core MCDD0003 in the McArthur Basin. Anoxic black shales in open-marine basins have been shown to record contemporaneous seawater $\varepsilon^{205}Tl_{sw}$ [3], which on geologically short timescales responds to isotopic fractionation during Tl adsorption to manganese oxides in well-oxygenated environments [4]. Thallium-205 is preferentially adsorbed to manganese oxides versus ^{203}Tl, shifting seawater to lighter ε^{205}Tl during periods of enhanced manganese oxide burial in more oxygenated oceans (modern $\varepsilon^{205}Tl_{sw}$ is –6, ocean inputs are –2). Thus, tracking $\varepsilon^{205}Tl_{auth}$ through the Wollogorang Formation may provide information on oxygenation at this time.

We observe two excursions to minimum $\varepsilon^{205}Tl_{auth}$ of –4.9 and –4.0 at ~55 m and ~30 m, respectively, from a baseline of –3 to –2 (Figure 1). Another recent study reported $\varepsilon^{205}Tl_{auth}$ near –5 over three metres in the Mount Young 2 core but may not reflect $\varepsilon^{205}Tl_{sw}$ due to possible post-depositional alteration [5]. In MCDD0003, there is evidence of sedimentary-exhalative (SEDEX) base-metal enrichment at ~40-50 m, a process that may shift $\varepsilon^{205}Tl_{auth}$ towards average oceanic input ε^{205}Tl. Basin restriction can also affect $\varepsilon^{205}Tl_{auth}$, but our geochemical data are not consistent with restriction-controlled $\varepsilon^{205}Tl_{auth}$ variations. We therefore propose two scenarios: (1) $\varepsilon^{205}Tl_{auth}$ reflects $\varepsilon^{205}Tl_{sw}$ and demonstrates two brief oxygenation periods ; (2) SEDEX processes reset $\varepsilon^{205}Tl_{auth}$ towards ocean input ε^{205}Tl, thus we cannot confirm whether the excursions were isolated or if $\varepsilon^{205}Tl_{sw}$ was continuously near –4. Hence, we infer at least occasional increased oxygenation within the McArthur Basin, and potentially the global oceans, at ~1.73 Ga.

[1] Parfrey et al. (2011), *PNAS* 108(33), 13624-13629.
[2] Javaux & Lepot (2018), *ESR* 176, 68-86.
[3] Wang et al. (2022), *GCA* 333, 347-361.
[4] Nielsen et al. (2013), *GCA* 117, 252-265.
[5] Li et al. (2021), *GCA* 315, 185-206.

Equation 1

$$\varepsilon^{205}Tl_{auth} = \left(\frac{^{205}Tl/^{203}Tl_{sample}}{^{205}Tl/^{203}Tl_{NIST3158}} - 1 \right) \times 10000$$

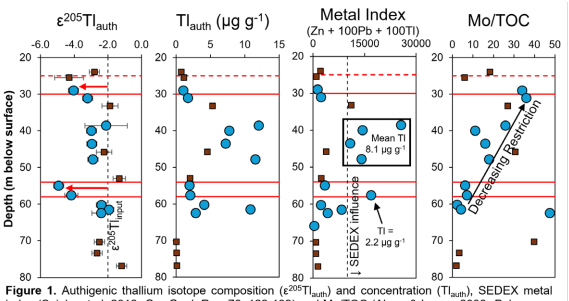

Figure 1. Authigenic thallium isotope composition ($\varepsilon^{205}Tl_{auth}$) and concentration ($Tl_{auth}$), SEDEX metal index (Spinks et al. 2016. *Ore Geol. Rev.* 76, 122-139) and Mo/TOC (Algeo & Lyons, 2006. *Paleocean.* 21(1), PA1016) profiles in the Wollogorang Formation drill core MCDD0003 in the McArthur Basin, NT, Australia. Larger blue circles depict samples that reflect contemporaneous seawater ε^{205}Tl based on the geochemical decision tree of Wang et al. (2022). Smaller brown squares are samples which reflect an ambiguous geochemical signature from the same decision tree.